

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**ScienceDirect**

Procedia Materials Science 8 (2015) 841 – 850

**Procedia**  
Materials Science[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)International Congress of Science and Technology of Metallurgy and Materials, SAM -  
CONAMET 2013

## Chlorination of RuO<sub>2</sub> with gaseous Cl<sub>2</sub> between 998 and 1123 K

Cristina N. Guibaldo<sup>a\*</sup>, Georgina De Micco<sup>a,b</sup>, Ana E. Bohe<sup>a,b,c</sup><sup>a</sup>*Comisión Nacional de Energía Atómica, Av. Bustillo 9500, S.C de Bariloche, Río Negro, Argentina*<sup>b</sup>*Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET, Argentina*<sup>c</sup>*Universidad Nacional del Comahue, Centro Regional Universitario Bariloche, Argentina*

### Abstract

Employing methods of separation based on selective chlorination it is possible to separate valuable components, such as metals and rare earths, from ores and / or solid wastes. In this paper we study the chlorination reaction of ruthenium oxide. This element is among nuclear fission products, also part of many electronic wastes and numerous catalysts in the chemical industry. The study of the chlorination reaction of ruthenium oxide will allow to analyze in which conditions it is possible to apply gaseous chlorination for ruthenium recovery. No systematic studies on the kinetics and chemical mechanism of ruthenium oxide chlorination are available in the literature. In the present study, we performed a thermodynamic analysis of possible reaction pathways. The reaction products were identified by scanning electron microscopy (SEM) and x-ray Diffraction (xrd), and the experimental conditions for obtaining stable  $\alpha$ -RuCl<sub>3</sub> by RuO<sub>2</sub> chlorination and subsequent heating in Cl<sub>2</sub> were established. The starting temperature for the chlorination was determined at 983 K. The observed mass loss is due to formation of volatile products. We analyzed the effects of gas flow rate, crucible geometry, and sample mass on the kinetics of the reaction, in order to establish the corresponding experimental reaction conditions for chemical kinetic control. The effect of temperature was analyzed and an apparent activation energy of  $173 \pm 8 \text{ kJ.mol}^{-1}$  was obtained for the chlorination reaction.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013

**Keywords:** ruthenium oxide; chlorination; kinetics; thermogravimetry.

\* Corresponding author.

E-mail address: [crisguibaldo@cab.cnea.gov.ar](mailto:crisguibaldo@cab.cnea.gov.ar)

## 1. Introduction.

The rapid population growth and urban concentration, the increase in industrial activity and consumption patterns, especially in developing countries, contribute to the serious problem of solid waste generation. Mishandling of this wastes directly affects environmental degradation and deterioration of public health. For that reason, it is important to develop strategies to minimize these negative effects and recover valuable elements contained in residues, so that they can be properly reinserted back into the consumption cycle.

A low abundance and high cost precious metal element belonging to the platinum group metals is ruthenium. This metal has many industrial uses in the electronics, chemistry and metallurgy Cotton (1997); Over (2012); Ran et al. (2013).  $\text{RuO}_2$  is used as a catalyst material for  $\text{Cl}_2$  production according to the Deacon reaction López et al. (2008), and in electrocatalysis where  $\text{RuO}_2\text{-TiO}_2$  coated titanium anodes are industrially used for chlorine evolution in  $\text{NaCl}$  electrolytic cells Panić et al. (1999); Arikawa et al. (1998). Especially in the last years, the range of applications has expanded rapidly. Recent applications include  $\text{RuO}_2$  thin films used as electrode materials in advanced memory technologies Musić et al. (2004), and all solid state supercapacitors for energy storage Dubal et al. (2013), among others.

Ruthenium chloride is a layered compound of interesting fundamental properties and increasing importance in surface science and chemistry. It is used in catalysis in organic synthesis Lowe (2007) and in nanocomposite hybrid materials Wang et al. (2000, 1998)

A possible methodology that could be employed to recover ruthenium from waste generated in the aforementioned applications, (i.e. spent catalysts and electronic scraps) and produce ruthenium chloride is dry chlorination. To design a recuperation process of that kind, a thorough understanding of the kinetics and reaction mechanism of the chlorination reactions implied in the recovery process, such as  $\text{RuO}_2$  chlorination is necessary.

The superficial physicochemical interaction between  $\text{RuO}_2\text{-HCl}$  and  $\text{RuO}_2\text{-Cl}_2$  at 623 K has been investigated in catalysts characterization studies Over (2012); Hevia et al. (2010). These authors reported the formation of stable oxychlorides  $\text{RuO}_{2-x}\text{Cl}_x$  only at surface level.

No information is available regarding the fundamental kinetic parameters and reaction mechanisms of the bulk chlorination reaction of  $\text{RuO}_2$  with gaseous chlorine. The present work is concerned with these aspects which are still unknown.

## 2. Methodology.

The gases used were Ar 99.99 % purity (AGA, Buenos Aires, Argentina) and  $\text{Cl}_2$  99.8 % purity (INDUPA, Buenos Aires, Argentina). As solid reagent, powder of  $\text{RuO}_2$  99.9 % purity (Sigma - Aldrich , Co., USA) was used. A BET area of  $9.8 \text{ m}^2 \text{ g}^{-1}$  for the  $\text{RuO}_2$  powder was determined with a Micromeritics analyzer (ASAP 2020). The materials were characterized by x-ray diffraction (XRD, Bruker D8 Advance), Scanning Electron Microscopy (SEM 515, Philips Electronic Instruments) and Energy Dispersive Spectroscopy (EDAX Genesis 2000). Isothermal and non isothermal chlorination reactions were conducted in a termogravimetric analyzer (TGA) especially adapted to work with corrosive atmospheres. It consists of an electrobalance, a gas line and an acquisition system. This system is constructed based on an electrobalance Cahn 2000. The electrobalance has a sensitivity of  $0.1 \text{ } \mu\text{g}$  and mechanical and electrical tares of 1 g and 100 mg respectively. The samples were placed in a quartz crucible hanging from a quartz wire in one of the arms of the balance. The mechanical tare hangs from the other arm of the balance. A vertical quartz tube leads the gases to the sample. The temperature of the sample was measured using a thermocouple Pt-Pt (10% Rh) encapsulated in quartz, which is located 5 mm below the crucible. This experimental system has a sensitivity of  $5 \text{ } \mu\text{g}$  operating at 1223 K (950 °C) with a flow rate of  $8 \text{ L h}^{-1}$ . Three sizes of containers were used to study the mass transfer of chlorine in the gas phase towards the solid sample, they consisted of quartz crucibles of different wall heights (0.9, 3.1 and 6.2 mm), hereinafter identified as low, medium and high crucible respectively. Samples of 0.5 to 5 mg of  $\text{RuO}_2$  were used. For non-isothermal measurements, the samples were heated in chlorine atmosphere at a heating rate of  $205 \text{ K h}^{-1}$ . For isothermal experiments, samples were heated for one hour in Ar up to the reaction temperature, and then the flow of chlorine was injected into the reactor. This procedure was employed to analyze the influence of the gas flow rate, initial mass of sample, type of crucible, and the temperature in the reaction rate.

Using separation of variables the reaction rate of a heterogeneous gas-solid reaction can be mathematically

described by J. Szekeley (1976):

$$\text{Rate} = \frac{d\alpha}{dt} = F(\alpha) \cdot K(T) \cdot F(P_{\text{Cl}_2}) \quad (1)$$

Where  $\alpha$  is the reaction degree defined as the ratio between the mass change and the initial mass  $((m_0 - m)/m_0)$ ,  $F(\alpha)$  is a function describing the geometric evolution of the solid during the reaction,  $K(T)$  is the temperature dependence according to the Arrhenius equation, and  $F(P_{\text{Cl}_2})$  expresses the dependence on chlorine partial pressure.

### 3. Results and Discussion.

#### 3.1. Initial $\text{RuO}_2$ characterization

$\text{RuO}_2$  is bluish black and has the crystal structure of rutile Cotton (1997). SEM images of the solid are shown in Figure 1(a), it can be seen that the grain size is in the order of nanometers. Figure 1(b) shows the diffraction pattern of a  $\text{RuO}_2$  sample, the peaks observed are in accordance with the corresponding reference pattern which is also shown in Figure 1(b).

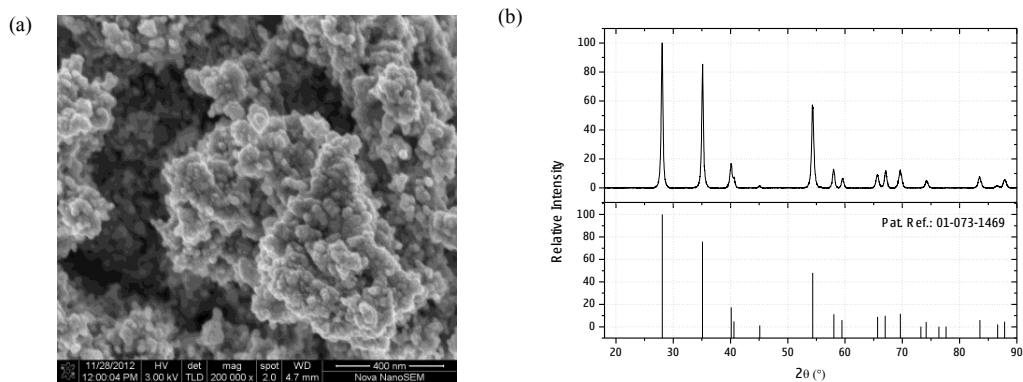
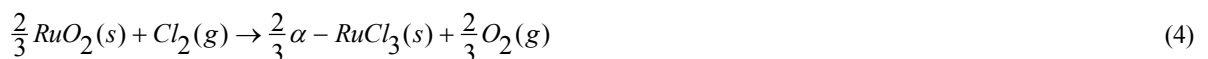


Fig. 1: (a) SEM image of initial  $\text{RuO}_2$ ; (b) XRD of initial  $\text{RuO}_2$

#### 3.2. Thermodynamical Analysis

The thermodynamic feasibility of different reactions between  $\text{RuO}_2$  and  $\text{Cl}_2$  was analyzed using the HSC Chemistry software Research (2007). The simulated experimental system was a gas-solid heterogeneous reaction. The following stoichiometric reactions were considered:



In the Ellingham diagram of Figure 2 it can be seen that no reaction is expected to proceed spontaneously and that equation 4 has the lower  $\Delta G^\circ$  value throughout the whole temperature range. However, considering that this reaction corresponds to formation of a solid product, it is to be expected that its accumulation would discourage the shift of this reaction towards product formation. The phase diagram (Figure 3(a)) indicates that in chlorine atmosphere (about 1 bar of  $p_{Cl_2}$  at 1173K) and very low partial pressure of oxygen ( $p_{O_2} = 10^{-20}$  bar) the  $\alpha$  phase of  $RuCl_3$  can be obtained.

Of all the reactions yielding gaseous products, equation 3 has the lower  $\Delta G^\circ$  value. In this case, the gaseous product is quickly removed by the gas stream which enhances the reaction towards products formation. Anhydrous  $RuCl_4$  has not been reported in solid state, it has been isolated only in hydrate form F.A. Cotton (1979). According to the reactions shown in Figure 3(b) when decreasing temperature, decomposition of  $RuCl_4$  into solid  $\beta$ - $RuCl_3$  would be feasible.

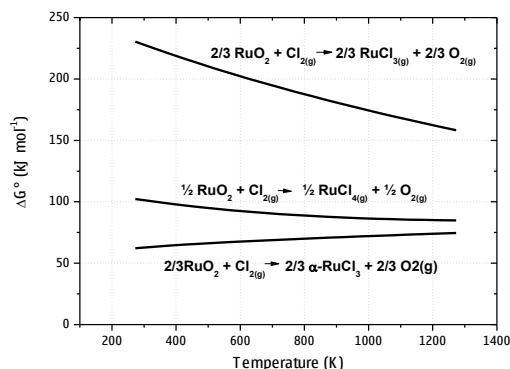


Fig. 2: Ellingham diagram for the chlorination of  $RuO_2$

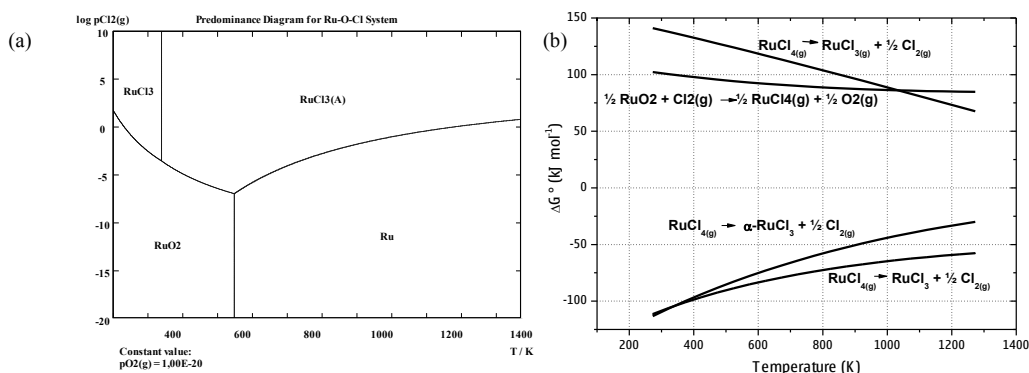


Fig. 3: (a) Predominance diagram for Ru-O-Cl system (b) Ellingham diagram for decomposition of  $RuCl_4$

### 3.3. Reaction Products Identification

In the thermogravimetric measurements presented below, sample mass loss is observed as the reaction progresses, which confirms the formation of gaseous products. To identify the products, the reaction was conducted in a tubular reactor which allows to condense and collect the vapors formed during the reaction. In the thermodynamic analysis, formation of ruthenium oxychlorides was not considered because thermodynamic data needed for equilibrium calculations are not available for these compounds. However it is not possible, at this point, to rule out formation of oxychlorides during chlorination reactions. The reaction product obtained is a dark brown and opaque condensate. It is unstable at ambient conditions, it is hydrolyzed in contact with atmospheric humidity and oxidized by

atmospheric oxygen. It is therefore necessary to work inside a glove box with controlled atmosphere conditions. X-ray diffraction was performed in a special sample holder suitable for hygroscopic samples built in the laboratory. Figure 4(a) shows the diffraction pattern obtained. The background observed indicates the presence of amorphous material, which may be due to instability of the sample even under the conditions used. Despite this, we could identify the presence of  $\beta$ - $\text{RuCl}_3$  Ref Pat.: 01-073-0319. The most intense peak corresponds to a  $\text{SiO}_2$  contamination from the reactor. Several oxychlorides had been claimed in the literature:  $\text{RuO}_{2-x}\text{Cl}_x$  Hevia et al. (2010),  $\text{Ru}_2\text{OCl}_4$ ,  $\text{Ru}_2\text{OCl}_6$  and  $\text{Ru}_2\text{OCl}_5$  F.A. Cotton (1979); K. Seki (2008, 2010). However, ruthenium oxychloride patterns are not reported in the database, with the only exception of  $\text{RuOCl}_2$  which does not match with the xrd profile obtained.

Hyde et al. (1965) investigated the differences between the structures of  $\alpha$  and  $\beta$  phases of  $\text{RuCl}_3$ . They found that the  $\beta$  phase is dark brown, opaque and has hygroscopic characteristics that match the sample obtained in this work. Some publications report the formation of  $\text{RuCl}_2$  by reaction of metallic ruthenium with  $\text{Cl}_2$  or  $\text{Cl}_2$ -CO mixture. However, such results are not clear Hyde et al. (1965). Steffen and Schllhorn (1986) characterized the  $\beta$ - $\text{RuCl}_3$  as strongly hygroscopic and easily soluble in water and polar organic solvents, and the  $\alpha$ - $\text{RuCl}_3$  as not soluble in such solvents Steffen and Schllhorn (1986).

The chlorination product was collected inside the glove box and was placed in a new silicon crucible, which was introduced back into a horizontal tubular reactor. A heat treatment was performed at 793 K (520 °C) in  $\text{Cl}_2$  atmosphere for 4 hours. After this, a black solid was obtained which is stable at atmospheric conditions, no volatilization was observed as solid deposition in the cold zone of the reactor. According to the literature, the  $\beta$  form of  $\text{RuCl}_3$  transforms into  $\alpha$  by heating at 723 K (450 °C) in  $\text{Cl}_2$  atmosphere. The latter phase has an appearance of very shiny black flakes, and a layered structure F.A. Cotton (1979). Figure 4 compares the xrd profiles of the reaction product (a) before and (b) after the heat treatment in chlorine. In Figure 4(b) it can be seen that the heat treated product is in accordance with the reference pattern 00-036-1225 of  $\alpha$ - $\text{RuCl}_3$ .

$\alpha$ -crystals of  $\text{RuCl}_3$  are shown in Figure 5. They consist of thin sheets of different sizes. In the picture on the right, hexagonal crystals of approximately 50  $\mu\text{m}$  in size can be seen. Steffen and Schllhorn (1986) obtained the same phase in the form of hexagonal thin single crystals by ruthenium chlorination. The crystals obtained by that reaction were larger (10 mm). The same authors found that the symmetry of the unit cell is hexagonal and the crystal structure is of the type  $\text{CdI}_2$  Steffen and Schllhorn (1986). The crystallographic system of  $\text{RuCl}_3$  diffraction pattern corresponding to the phase obtained by us is not reported.

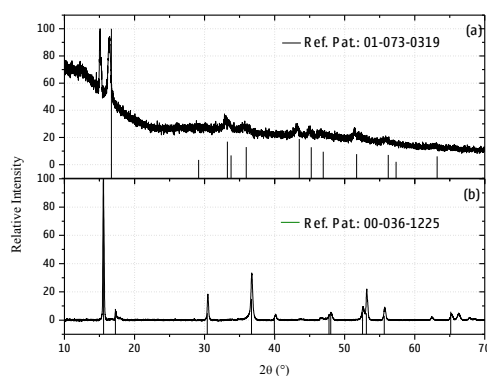


Fig. 4: (a) Reaction product of  $\text{RuO}_2$  chlorination; (b) Reaction product after thermal treatment in  $\text{Cl}_2$ .

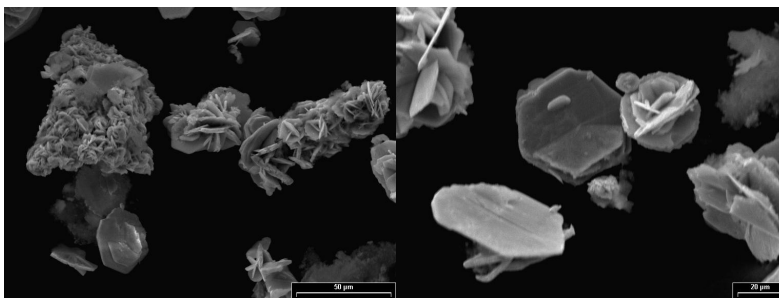


Fig. 5: SEM images of  $\alpha$ -RuCl<sub>3</sub> crystals.

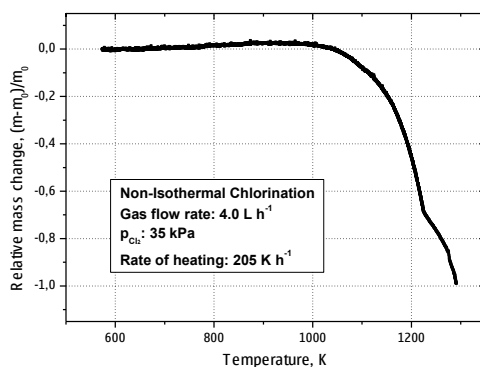


Fig. 6: Non isothermal chlorination of RuO<sub>2</sub>.

### 3.4. Thermogravimetric Analysis

The starting temperature for RuO<sub>2</sub> chlorination reaction was determined by non-isothermal thermogravimetric (TG) measurement. Figure 6 shows the mass change relative to the initial mass of the sample as a function of temperature. The reaction starts at about 983 K (710 °C) where the beginning of the mass loss was observed. The relative mass increase observed before that temperature is due to variations in gas density caused by the temperature increase.

To identify the reaction conditions in which the reaction rate is controlled by intrinsic chemical kinetics, the effects of gas flow rate, crucible geometry and initial sample mass were studied. For the gas flow it was obtained that the reaction rate ( $d\alpha/dt$ ) is independent of the flow for values greater than 4 L h<sup>-1</sup> for temperatures up to 1073 K (800 °C). However, for the crucible wall height (Figure 7) and the initial mass of sample (Figure 8), decreasing the wall height and the sample mass to the corresponding minimum possible values in the experimental system was not enough to achieve independence of the reaction rate. These results indicate that gaseous mass transfer affects the reaction rate and so the kinetic parameter calculated (activation energy) corresponds to an apparent value and not to the intrinsic value of the chemical reaction.

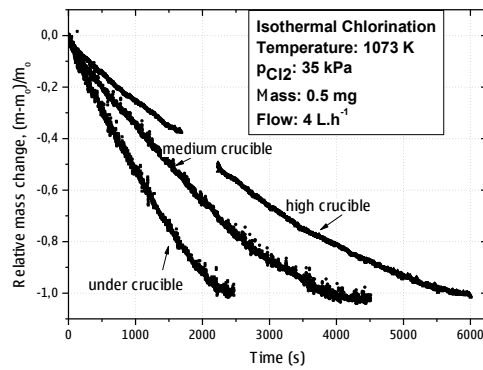


Fig. 7: TG curves for the isothermal chlorination of  $\text{RuO}_2$  with different crucibles.

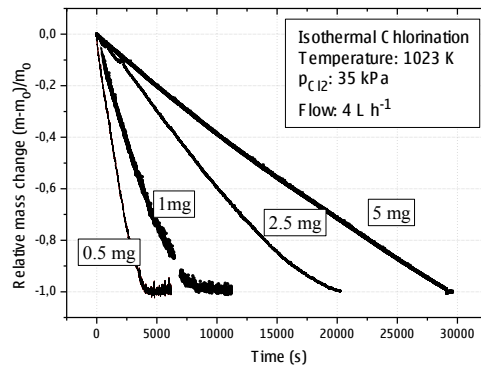


Fig. 8: TG curves for the isothermal chlorination of  $\text{RuO}_2$  with different sample masses (medium crucible).

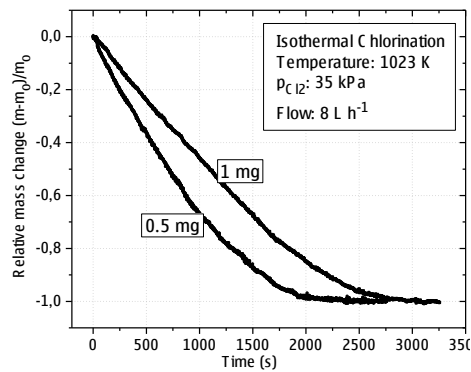


Fig. 9: TG curves for the isothermal chlorination of  $\text{RuO}_2$  with different sample masses (low crucible).

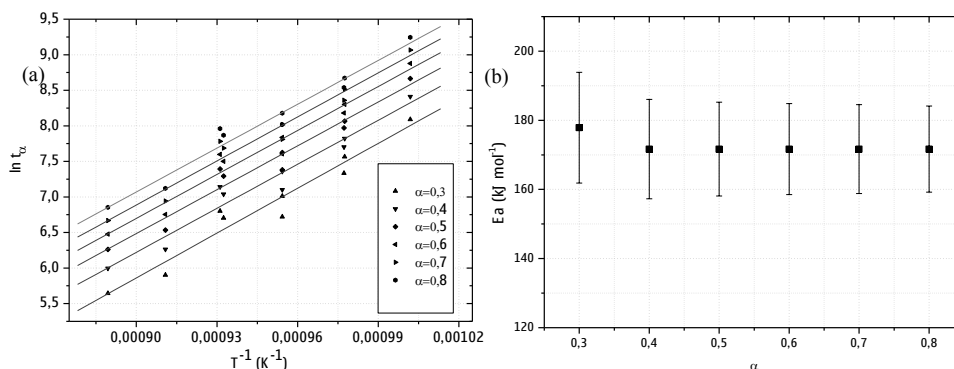


Fig. 10: (a)  $\ln t_\alpha$  vs  $T^{-1}$  plot for  $\alpha$  between 0.3 and 0.8; (b)  $E_a$  for different  $\alpha$  values with error bars.

Figure 7 shows the effect of crucible height. Reducing the wall's height lowers the rate of gaseous transfer of reactant towards the surface of the sample (because the thickness of the fluidynamic boundary layer around the crucible decreases). Consequently, the low crucible shows the highest rate of conversion. Figure 8 shows the TG curves for the chlorination of different initial masses of  $RuO_2$  using the medium crucible. An increase in the reaction rate when decreasing the sample mass can be seen. The velocity values obtained for initial masses of 1 and 0.5 mg differ by a value greater than the instrumental scattering, thus, this difference cannot be neglected. For the low crucible (Figure 9) an increase in the reaction rate (greater than the experimental scattering) was also observed when decreasing the sample mass. It is not possible to work with initial masses lower than 0.5 mg since measurements are not reproducible.

Isothermal chlorination reactions were carried out between 998 and 1123 K (725 and 850 °C), with 0.5 mg of initial mass, 4 L  $h^{-1}$  of gaseous flow and 35 kPa of  $Cl_2$  partial pressure. The reactions were performed with the medium crucible because it has better reproducibility. Rearranging Equation 1, and integrating up to different reaction degree values ( $\alpha$ ) and the corresponding values of time required to reach that degree of conversion ( $t_\alpha$ ), the activation energy from the slope of the  $\ln t_\alpha$  vs  $T^{-1}$  plot can be obtained Flynn (1988).

$$\ln t_\alpha = \frac{E_a}{RT} + \ln A \quad (5)$$

Where  $E_a$  is the activation energy,  $R$  is the universal gas constant,  $A$  a constant, and  $T$  the reaction temperature. Figure 10(a) shows the linear fit of the data for different values of  $\alpha$ .

Figure 10(b) shows the activation energy and the calculated fitting error for each value of  $\alpha$ . An average activation energy of  $173 \pm 8 \text{ kJ mol}^{-1}$  were calculated. Since the reaction rate is influenced by mass transfer in the gas phase and as all oxide chlorination reactions for which thermodynamic data are available have positive  $\Delta G^\circ$  values, i.e. small equilibrium constant, the apparent activation energy value should approximate the standard enthalpy change of reaction Sohn (2004). However, the value obtained is not consistent with the values of enthalpy change corresponding to equations 2 and 3 raised in section 3.2. This difference could be indicating that during the chlorination, gaseous oxychlorides for which thermodynamic data are not available, are also being formed.

#### 4. Conclusions.

In the present work we studied the chlorination reaction of  $RuO_2$  whose kinetics and mechanism is not reported in the literature. The starting temperature for the reaction associated with the reactivity of the oxide, was determined at 983 K (710 °C). A thermodynamic analysis was performed to determine the feasibility of the reaction and the expected chlorination products. Products obtained from the chlorination reaction at temperatures between 998 and 1123 K (725 and 850 °C) are volatile, so it was necessary to perform experiments in reactors that allow condensating and collecting the vapours for identification. Due to the instability of this condensate with respect to moisture and oxygen, it was necessary to work under atmosphere controlled conditions.  $\beta$ - $RuCl_3$  could be



identified as one of the reaction products. The presence of oxychlorides could not be confirmed so far. By heat treatment in chlorine atmosphere of the reaction products (maintained under controlled atmosphere) the stable phase  $\alpha$ -RuCl<sub>3</sub> was obtained. Hexagonal crystals were observed with a size of about 50 microns. The kinetics of the chlorination reaction was investigated and a value of the apparent activation energy of  $173 \pm 8 \text{ kJ mol}^{-1}$  was obtained. Being a reaction with small equilibrium constant and affected by the mass transfer, this value could correspond to  $\Delta H^\circ$  of oxychloride formation reaction or a combination of chlorides and oxychlorides.

## Acknowledgements

The authors would like to thank the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Universidad Nacional del Comahue for the financial support of this work.

## References

- Arikawa, T., Murakami, Y., Takasu, Y., 1998. Simultaneous determination of chlorine and oxygen evolving at RuO<sub>2</sub>/Ti and RuO<sub>2</sub>TiO<sub>2</sub>/Ti anodes by differential electrochemical mass spectroscopy. *Journal of Applied Electrochemistry* 28, 511-516. URL: <http://dx.doi.org/10.1023/A%3A1003269228566>, doi:10.1023/A:1003269228566.
- Cotton, S.A., 1997. *Chemistry of precious metals*. Chapman & Hall.
- Dubal, D.P., Gund, G.S., Holze, R., Jadhav, H.S., Lokhande, C.D., Park, C.J., 2013. Solution-based binder-free synthetic approach of RuO<sub>2</sub> thin films for all solid state supercapacitors. *Electrochimica Acta* 103, 103-109. URL: <http://www.sciencedirect.com/science/article/pii/S0013468613007123>, doi:10.1016/j.electacta.2013.04.055.
- F.A. Cotton, G.W., 1979. *Química Inorgánica Avanzada*. México: LIMUSA.
- Flynn, J., 1988. Thermal analysis kinetics-problems, pitfalls and how to deal with them. *Journal of thermal analysis* 34, 367-381. URL: <http://dx.doi.org/10.1007/BF01913405>, doi:10.1007/BF01913405.
- Hevia, M.A.G., Amrute, A.P., Schmidt, T., Pérez-Ramírez, J., 2010. Transient mechanistic study of the gas-phase HCl oxidation to Cl<sub>2</sub> on bulk and supported RuO<sub>2</sub> catalysts. *Journal of Catalysis* 276, 141-151. URL: [www.scopus.com](http://www.scopus.com). cited By (since 1996):23.
- Hyde, K., Hooper, E., Waters, J., Fletcher, J., 1965.  $\alpha$ - and  $\beta$ -ruthenium trichloride. *Journal of the Less Common Metals* 8, 428-434. URL: <http://www.sciencedirect.com/science/article/pii/0022508865900822>, doi:10.1016/0022-5088(65)90082-2.
- J. Szekely, J.W. Evans, H.S., 1976. *Gas-solid reactions*. New York: Academic Press.
- K. Seki, E.N.S., 2008. Method for production of supported ruthenium and method for production of chlorine. Technical Report. Patent N: EP 1 958 693 A1.
- K. Seki, J.N., 2010. Process for producing supported ruthenium and process for producing chlorine. Technical Report. Patent N: US 7 858 065 B2.
- López, N., Gómez-Segura, J., Marn, R.P., Pérez-Ramírez, J., 2008. Mechanism of HCl oxidation (deacon process) over RuO<sub>2</sub>. *Journal of Catalysis* 255, 29-39. URL: <http://www.sciencedirect.com/science/article/pii/S0021951708000353>, doi:10.1016/j.jcat.2008.01.020.
- Lowe, J.T., 2007. Ruthenium-chloride RuCl<sub>3</sub>. *Synlett* 2007, 1974-1975. URL: <https://www.thieme-connect.com/ejournals/abstract/10.1055/s-2007-984876>, doi:10.1055/s-2007-984876.
- Musić, S., Popović, S., Maljković, M., Sarić, A., 2004. Synthesis and characterization of nanocrystalline RuO<sub>2</sub> powders. *Materials Letters* 58, 1431-1436. URL: <http://www.sciencedirect.com/science/article/pii/S0167577X03007985>, doi:10.1016/j.matlet.2003.09.040.
- Over, H., 2012. Surface chemistry of ruthenium dioxide in heterogeneous catalysis and electrocatalysis: From fundamental to applied research. *Chemical Reviews* 112, 3356-3426. URL: <http://pubs.acs.org/doi/abs/10.1021/cr200247n>, doi:10.1021/cr200247n, arXiv:10.1021/cr200247n, <http://pubs.acs.org/doi/pdf/10.1021/cr200247n>.
- Panić, V., Dekanski, A., Milonjić, S., Atanasoski, R., Nikolić, B., 1999. RuO<sub>2</sub>TiO<sub>2</sub> coated titanium anodes obtained by the sol-gel procedure and their electrochemical behaviour in the chlorine evolution reaction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 157, 269-274. URL: <http://www.sciencedirect.com/science/article/pii/S0927775799000941>, doi:10.1016/S0927-7757(99)00094-1.
- Ran, L., Qin, Z., Wang, Z., Wang, X., Dai, Q., 2013. Catalytic decomposition of {CH<sub>2</sub>Cl<sub>2</sub>} over supported Ru catalysts. *Catalysis Communications* 37, 5-8. URL: <http://www.sciencedirect.com/science/article/pii/S1566736713001003>, doi:10.1016/j.catcom.2013.03.017.
- Research, O., 2007. HSC Chemistry software version 6.12. Oy, Pori, Finland.
- Sohn, H., 2004. The effects of reactant starvation and mass transfer in the rate measurement of fluid-solid reactions with small equilibrium constants. *Chemical Engineering Science* 59, 4361-4368. URL: <http://www.sciencedirect.com/science/article/pii/S0009250904004208>, doi:10.1016/j.ces.2004.06.033.
- Steffen, R., Schllhorn, R., 1986. Intercalation reactions of ruthenium-(III)-chloride via electron/ion transfer. *Solid State Ionics* 22, 31-41. URL: [www.scopus.com](http://www.scopus.com). cited By (since 1996):8.
- Wang, L., Brazis, P., Rocci, M., Kannewurf, C.R., Kanatzidis, M.G., 1998.  $\alpha$ -RuCl<sub>3</sub>: a new host for polymer intercalation. lamellar polymer/ $\alpha$ -RuCl<sub>3</sub> nanocomposites, in: *Materials Research Society Symposium - Proceedings*, pp. 257-264. URL: [www.scopus.com](http://www.scopus.com). cited By (since 1996):4.

Wang, L., Rocci-Lane, M., Brazis, P., Kannewurf, C.R., Kim, Y., Lee, W., Choy, J., Kanatzidis, M.G., 2000.  $\alpha$ -RuCl<sub>3</sub>/polymernanocomposites: The first group of intercalative nanocomposites with transition metal halides. *Journal of the American Chemical Society* 122, 6629-6640. URL: [www.scopus.com](http://www.scopus.com). cited By (since 1996):61.